Mesoporous Hollow SiO_2 Spheres Stabilized Pickering Emulsion to Improve Water Vapor Permeability and Water Resistance for Leather Finishing Agent

Yan Bao[1, 3*], Yuanxia Zhang[1, 2*] and Jianzhong Ma [1, 3*]

1 College of Bioresources Chemical and Materials Engineering, Shaanxi University of Science and Technology, Xi'an, 710021, PR, China.

2 National Demonstration Center for Experimental Light Chemistry Engineering Education, Shaanxi University of Science and Technology, Xi'an, 710021, PR, China.

3 Shaanxi Research Institute of Agricultural Products Processing Technology, Xi'an, 710021, PR, China.

1) Corresponding author: Yan Bao, E-mail: baoyan@sust.edu.cn

2)Jianzhong Ma, E-mail: majz@sust.edu.cn

Abstract. In order to solve the negative impact of coating on water vapor permeability of leather and overcome the poor water resistance of polyacrylate leather finishing agent, it was proposed that the mesoporous SiO_2 spheres with hollow structure instead of traditional surfactant were introduced into polyacrylate by Pickering emulsion polymerization. It was expected to increase the water vapor permeability of polyacrylate membrane by increasing the path and shortening the route of water vapor molecules through the membrane, and improve the water resistance of membrane by avoiding the use of surfactant. Hence, stable Pickering emulsion stabilized by mesoporous hollow SiO_2 spheres was prepared and its stability was investigated by Turbiscan Lab in this paper. Water vapor permeability and water uptake of polyacrylate membrane were also studied. Compared with emulsion stabilized by surfactant, Pickering emulsion indicated excellent stability with lower TSI value of 0.5. Contrasted with polyacrylate membrane with SDS, the introduction of mesoporous hollow SiO_2 spheres can improve the water vapor permeability of polyacrylate membrane. Meanwhile, water absorption measurements showed that the water absorption ratio of the membrane with mesoporous hollow SiO_2 spheres reduction of down to 40.84%, possessing the ideal ability to water resistance of polyacrylate membrane. This study can provide a theoretical foundation for designing and synthesizing leather finishing agent with excellent stability, water vapor permeability and water resistance synchronously.

Keywords: Pickering emulsions; mesoporous hollow SiO_2 spheres; stability; water vapor permeability; water resistance

1 Introduction

Water vapor permeability of coating for leather is of great importance when the leather is used for the shoes and clothes [1]. In order to keep human bodies comfortable, shoes and clothes should have high water vapor permeability value, which allows perspiration to evaporate promptly, especially when people are in hot environments.

Up to date, many effects to improve the hygienic performance of leather have been done. In the study conducted by Zheng et al., high water vapor permeable porous materials were prepared by polyporous coating, blending of waterborne polyurethanes (WPUs) and polyacrylate (AC) on fabrics [2]. It revealed that the introduction of hydrophilic groups can significantly improve the moisture permeability of the membrane, but the presence of hydrophilic groups of AC will lead to the poor water resistance. Wu et al. improve the water vapor permeability of polyurethane membranes by increasing the number of micropores in the membrane [3]. It can obviously enhance water vapor permeability of coating. Unfortunately, those ideals have only focus on polyurethane and polymer fiber. There are few studies on water vapor permeability using polyacrylate, although polyacrylate is commonly used in leather. Of particular note, polyacrylate emulsions by emulsion polymerization always show poor water resistence on account of the presence of surfactant.

Inspired by those results, physical blending of hollow SiO_2 spheres and polyacrylate has been proposed to provide pores for the water vapor molecules' passing in our work [4]. Most interestingly, compared with pure polyacrylate membrane, the water vapor permeability of polyacrylate membrane containing mesoporous hollow SiO_2 spheres is improved greatly. Besides, in the latest study conducted by Yang et al., mesoporous SiO_2 microspheres stabilized Pickering emulsion was reported. It possessed outstanding stability against coalescence, suggesting that the internal pores of particles had positive impacts on the stability of Pickering emulsions [5]. To obtain Ideal polyacrylate leather finishing agent, which possesses excellent stability, water vapor permeability and water resistance synchronously, we aim to fabricate mesoporous hollow SiO_2 spheres stabilized Pickering emulsion. We will deduce the positive effect of the introduction of mesoporous hollow SiO_2 spheres for the stability of polyacrylatee mulsion and the water vapor permeability and water resistance of polyacrylate coating for leather.

2 Results and Discussion

As is known, the stability is a key for the property of emulsion. Firstly, the stability of mesoporous hollow SiO_2 spheres stabilized Pickering emulsion has been investigated by Turbiscan Lab Expert. The turbiscan stability index (TSI) was further calculated from the experimental results (Program Turbiscan Easy Soft) using the following equation (1) [6]. Generally, a low value of TSI indicates the ideal stability of polyacrylate emulsion [7].

$$\mathrm{TSI} = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_{BS})^2}{n-1}} \qquad (1)$$

Where: x_i is the mean backscattering and transmission of each scan in experiment, x_{BS} is the mean x_i, and n is the number of scans.

It can be seen that the TSI value (Fig. 1b) of polyacrylate emulsion stabilized by SDS changes quicker within 5h. While mesoporous hollow SiO_2 spheres stabilized polyacrylate emulsion exhibits the smaller change and lower TSI value of in Fig. 1b (The maximum TSI value of 0.5). Compared with emulsion stabilized by surfactant, mesoporous hollow SiO_2 spheres stabilized Pickering emulsion indicates excellent stability. It further reveals that mesoporous hollow SiO_2 spheres possess higher adsorption energy at the oil-water interface so that they possess excellent ability to against droplets coalescence.

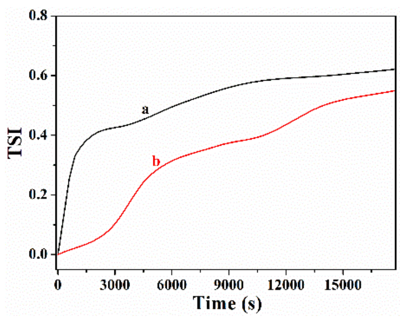

Fig. 1. Time dependence of the stability coefficient TSI of polyacrylate emulsion stabilized by different stabilizers: (a) stabilized by conventional surfactant SDS, (b) stabilized by mesoporous hollow SiO_2 spheres.

In order to clearly understand the effect of mesoporous hollow SiO_2 spheres on water vapor permeability of membrane, water vapor permeability of polyacrylate membrane with SDS as a comparison has been investigated. Of particular interest, the water vapour permeability of membrane with mesoporous hollow SiO_2 spheres is higher than that of membrane with SDS. It shows the introduction of mesoporous hollow SiO_2 spheres can enhance water vapour permeability of membrane. This is because mesoporous hollow SiO_2 spheres further introduce a lot of free volume in the membrane due to their hollow core, which provide many channels for water vapor. Meanwhile, a small amount of water vapor from the hollow core of SiO_2 spheres can bring a water vapor pressure difference between inside and outside of SiO_2 spheres, enhancing water vapour permeability [8].

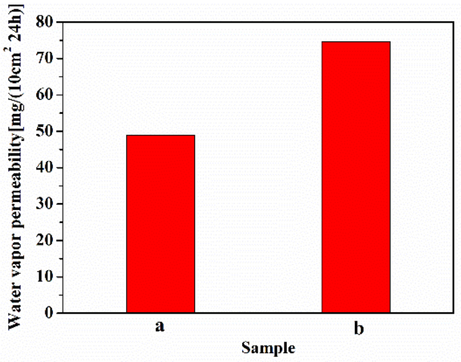

Fig. 2. Water vapor permeability of polyacrylate membranes (a) SDS stabilized polyacrylate emulsion; (b) mesoporous hollow SiO_2 spheres stabilized polyacrylate emulsion.

Further, it can be seen in Fig 3 that water resistance of polyacrylate membrane with SDS is the worst. It is because that surfactant containing hydrophilic group will migrate to the membrane surface in the process of membrane forming and make the water molecules are more likely to enter the membrane inside. However, polyacrylate membrane with mesoporous hollow SiO_2 spheres show water absorption of 40.84%, possessing the ideal ability to water resistance of polyacrylate membrane. Better water resistance also accounts for the strong interfacial adsorption interaction between mesoporous hollow SiO_2 spheres and polyacrylate latex particles.

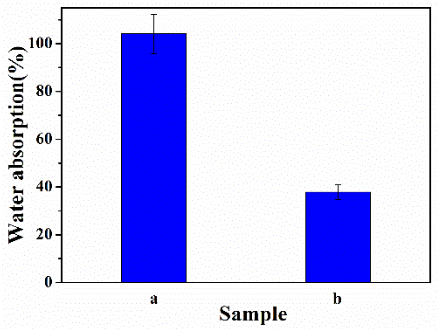

Fig. 3. The water uptake of polyacrylate membranes (a) SDS stabilized polyacrylate emulsion; (b) mesoporous hollow SiO_2 spheres stabilized polyacrylate emulsion.

In summary, mesoporous hollow SiO_2 spheres stabilized polyacrylate emulsion was successfully obtained. The results show that mesoporous hollow SiO_2 spheres stabilized polyacrylate emulsion has excellent stability. The effect of hollow SiO_2 spheres on water vapor permeability and water uptake of polyacrylate membrane were investigated. It indicates that hollow SiO_2 spheres can significantly improve water vapor permeability of polyacrylate membrane, and enhance its water resistance. Overall, this study not only provides a novel ideal stabilizer for the fabrication of polyacrylate emulsion, but also reveals that as-prepared polyacrylate/hollow SiO_2 membrane maybe found potential applications in coatings for leather.

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